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Numerical simulation of particle formation in the rapid expansion of supercritical solution process

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ABSTRACT

In this paper, we numerically study particle formation in the rapid expansion of supercritical solution (RESS) process in a two dimensional, axisymmetric geometry, for a benzoic acid + CO_2 system. The fluid is described by the classical Navier–Stokes equation, with the thermodynamic pressure being replaced by a generalized pressure tensor. Homogenous particle nucleation, transport, condensation and coagulation are described by a general dynamic equation, which is solved using the method of moments. The results show that the maximal nucleation rate and number density occurs near the nozzle exit, and particle precipitation inside the nozzle might not be ignored. Particles grow mainly across the shocks. Fluid in the shear layer of the jet shows a relatively low temperature, high nucleation rate, and carries particles with small sizes. On the plate, particles within the jet have smaller average size and higher geometric mean, while particles outside the jet shows a larger average size and a lower geometric mean. Increasing the preexpansion temperature will increase both the average particle size and standard deviation. The preexpansion pressure does not show a monotonic dependency with the average particle size. Increasing the distance between the plate and the nozzle exit might decrease the particle size. For all the cases in this paper, the average particle size on the plate is on the order of tens of nanometers.

1. Introduction

Fine and monodisperse particles are important in many applications, such as production of pharmaceuticals, dyes and ceramic processing, pigments in paint formulation [1], as well as surface coating [2–4]. There are conventional technologies to reduce the particle size, but these have drawbacks. One is mechanical methods like grinding, milling and crushing, but many solids are difficult to comminute mechanically. Another is the equilibrium-controlled method like liquid phase crystallization, for which a high purity product is hard to obtain. In addition, the sizes of particles obtained from those conventional methods are always nonuniform [1]. The rapid expansion of supercritical solutions (RESS) process, which has received increased attention in the past years, is an innovative and promising method to produce small particles with narrow size distribution [5]. In the RESS process, a supercritical solution at moderate pressure is sprayed from a nozzle into an expansion chamber where the pressure is much lower, and thus the solution expands rapidly. The solvating strength of supercritical fluids is directly related to the fluid density. Generally speaking, the higher the density, the stronger the solvating power [6,7]. The rapid expansion in the RESS process leads to a rapid decrease in the solvent's density and solvating strength, resulting in solute precipitation and the formation of fine particles. Those particles will be collected on a plate which is positioned in front of the spray nozzle.

The most common supercritical solvent is carbon dioxide (CO_2). It has several advantages. First, it has low critical temperature ($T_c = 304.1282$ K) and mild critical pressure ($p_c = 7.3773$ MPa), which makes its supercritical state easy to reach. Second, it is non-toxic, non-flammable and environmentally friendly, it is also widely available and low-cost. Third, it is in a gaseous state under atmospheric conditions, so the final product is solvent free and has a high purity.

Experimental research on the RESS process has been conducted for over 20 years [5], but numerical simulation of the RESS process is still in an early state, and most of the published studies are 1-dimensional (1D). A recent review of numerical investigations regarding supercritical fluid expansion can be found in the work of Moussa and Ksibi [8]. In the following, we are going to briefly review some previous numerical works, first for 1D, and then for 2D.

Debenedetti, Kwauk and others investigated particle formation during the partial expansion of a dilute supercritical mixture in a convergent nozzle under subsonic conditions both experimentally and numerically [1,9,10]. They modeled the flow field as a

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one-dimensional steady flow with Peng–Robinson equation of state (EoS), and the particles by the general dynamic equation (GDE) equation. Particle nucleation and condensation is included in this model, while coagulation is neglected since the typical residence time within their simulation domain is much less than the estimated coagulation times. They showed that increasing the pre-expansion temperature would increase particle size while increasing extraction temperature would decrease particle size. They also showed that small changes in surface tension could result in large variations in the predicted particle size. Weber, Russell, and Debenedetti included coagulation mechanics for particle growth in later publications [11], in which an aerosol dynamic equation was solved with a sectional method along an expansion device. But the particles' sizes found in their experiments were much larger than their numerical results, which might be due to limitations of their model.

In a series of papers [12,5,13,14], Türk, Helfgen and others studied particle formation in the RESS process both experimentally and numerically, for various solutes in different supercritical solvents. The solution they considered is very dilute. They modeled the pure solvent by a one-dimensional, steady state fluid model, and the extended generalized Bender (egB) equation of state was used to close the system. The particle formation process was modeled by the GDE, considering homogenous nucleation, condensation and coagulation effects all together. The GDE was solved by the moment's method. Their simulation domain included the convergent capillary inlet, the straight nozzle and the large expansion chamber part. They showed [5] that the supersaturation and nucleation rate was very sensitive to the solubility and surface tension of the solute-solvent system, and the classical nucleation theory was not suitable to describe the trend in particle size. The general trends of their numerical results [14] showed good agreement with experiments, but the predicted particle sizes didn't match the measured particle sizes exactly. Their later work [13] showed that particle formation occurs mainly in the supersonic free jet and coagulation was the main mechanism for particle growth.

Other one-dimensional numerical works include Lele et al. [15], Reverchon and Palado [16], Weber and Thies [17], etc. 1D simulations are good attempts to uncover and understand physics in RESS, like the thermodynamic conditions along the centerline. But they might not be able to completely represent the physics of the flow since it cannot capture the processes that happen off-axis, like the large gradient of the thermal conditions in the oblique shock originating from the lip of the nozzle exit. Thus, 1D simulations might be insufficient if we want to explain the experimental results well.

Ksibi and Moussa's group published several papers about numerical simulations on the RESS process in 2D, axisymmetric geometry. Ksibi et al. [18] investigated the rapid expansion of pure supercritical CO_2 by modeling it as a Newtonian, viscous compressible fluid, governed by the Navier–Stokes equation, and satisfying the Altumin and Gadetskii equation of state [19]. The system of equations were solved by the Total Variation Diminishing scheme using a finite difference method, with Roe averaged technique [20] for shock capture. Their studies focused on the profiles of thermodynamic variables along the centerline and the normal plate, when the pure supercritical carbon dioxide expanded into the expansion chamber which contained motionless pure carbon dioxide. Following Ksibi's work, Moussa et al. [21] carried out a parametric study of the nozzle geometry to control the supercritical fluid expansion for carbon dioxide. They showed that the geometry of the nozzle and operating condition would highly influence the jet structure.

The aforementioned 2D simulations did not consider particle formation during the RESS process. In 2008, Moussa et al. [22] incorporated particle formation in their two dimensional, axisymmetric supersonic jet during the RESS process. Particle transport and growth were governed by the time dependent aerosol GDE, without considering nucleation and condensation. A lognormal size distribution function was assumed for the particles and the GDE was solved with a sectional method. They found that particles deposit on the flat plate as a ring since particles located at the jet boundary are subjected to more pronounced Brownian coagulation. They also found that a larger orifice and lower expansion pressure leads to a narrower distribution of particles on the flat plate.

Other 2D numerical simulation works on RESS are: Franklin et al. [23] numerically simulated the rapid expansion of the perfluoropolyether–carbon dioxide supercritical solution into air by solving an axisymmetric, Favre-averaged compressible Navier–Stokes equations which was suitable for turbulent flow simulations. The ideal-gas law was applied for the air, and gas-phase mixing rule was applied between CO_2 and air. The lattice-fluid state equation of Sanchez and Lacombe was used for both single-phase CO_2 and the solute perfluoropolyether diamide, which was in a liquid state at the conditions of interest. Separate continuity equations were used for air and CO_2. Khali et al. [24] studied the structure of supercritical jet expansion for in viscid, adiabatic pure carbon dioxide flow impacting on a flat plate, but particle formation was not considered. They solved an axisymmetric Euler equation with the Redlich–Kwong equation of state [25], using a two-step Lax–Wendroff finite difference method. They showed that their numerical results compared reasonably well with their experiment if the pressure was not very high. They proposed that a divergent-convergent capillary could be more suitable for the RESS process than a convergent nozzle. Dea et al. [26] investigated the growth of magnetic thin films using carbon dioxide RESS expansion, following the 2D work of Khali et al. [24]. They applied a quasi-one dimensional analysis to thermal properties on the jet centerline, and a kinematic model for the particle formation, which was based on bimolecular collisions.

Numerical studies of particle formation in the RESS process are still in an embryonic state [22]. Existing numerical simulations can only roughly interpret the experimental results, sometimes they even contradict experimental results [5]. In order to gain a better understanding of this process and provide some guidance in experimental design to produce small and uniform particles, we numerically study particle formation in the RESS process in a 2D, axisymmetric geometry for CO_2-benzoic acid system. The fluid is described by the classical Navier–Stokes equation, with the usual pressure term being replaced by the generalized pressure tensor [27]. The equation of state is the egB equation of state [5,28].

For the particle model, following previous work of Pratsinis [29] and Helfgen et al. [14], the method of moments is used to solve the general dynamic equation, which accounts for the aerosol dynamics during a simultaneous particle nucleation, condensation and coagulation process. We are going to first study a typical case in detail, and then do a parametric study, to see how things change when we change the preexpansion temperature, the preexpansion pressure and the plate position.

The rest of the paper is organized as follows: Section 2 describes the models, including the fluid dynamic equations in Section 2.1 and the particles model in Section 2.2, as well as the moment equations in Section 2.3. In Section 3, we talk about the numerical method, show some numerical results, and discuss some issues. Section 4 is the conclusion. Section 5 is the acknowledgement. Section A is the appendix.

2. Problem formulation

The governing equations consist of two parts. One is the fluid dynamic equations, which describe the evolution of density, temperature, pressure and velocity of the flow. The other is the general dynamic equation, which models the evolution of the number density of the particles in the whole domain. The general dynamic

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